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Preparation of Polymer−Silicon(100) Hybrids via Interface-Initiated Reversible Addition-Fragmentation Chain-Transfer (RAFT) Polymerization

Qiang Peng,[†] Doreen M. Y. Lai,[‡] E. T. Kang,*[,†] and K. G. Neoh[†]

Department of Chemical and Biomolecular Engineering, National University of Singapore, Kent Ridge, Singapore 119260, Singapore, and Institute of Materials Research and Engineering, National University of Singapore, 3 Research Link, Singapore 117602, Singapore

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Introduction

Functionalization of semiconductor surfaces can be achieved through immobilization of organic molecules and polymer brushes.[1,2] Covalent attachment of polymer chains to a surface can be accomplished by either the “grafting to” or “grafting from” technique.[3−6] Hybrids consisting of covalently attached organic molecules or polymer brushes on oriented single-crystal silicon surfaces via Si−C bonds are attractive, because of the robustness of the Si−C bonds.[7−12] Well-defined polymer brushes have been immobilized on various substrates via living radical polymerizations, including nitroxide-mediated radical polymerization (NMP),[13,14] atom transfer radical polymerization (ATRP),[15−17] and reversible addition−fragmentation chain transfer (RAFT) polymerization.[18,19] A number of studies have dealt with the modification of oriented single-crystal silicon surfaces by ATRP.[20−26] RAFT polymerization is another versatile technique due to its compatibility with a wide range of monomers and reaction conditions.[27] Relatively few studies have been devoted to the modification of oriented single-crystal silicon surfaces by the RAFT process.[18,28,29] In most cases, the chain transfer agent (CTA) is attached through the leaving and reinitiating group (R group), resulting in a “grafting from” process. The process resembles that of surface-initiated ATRP from a surface-anchored initiator. Recently, several fine studies on RAFT polymerization agents anchored on silica nanoparticles,[30] cadmium selenide nanoparticles,[31] Merrifield resin,[32] and cellulose[33] have been reported.

In this work, we report on the surface modification of (100)-oriented single-crystal silicon with covalently bonded (Si−C bonded) polymer brushes by interface-mediated RAFT polymerization, with the CTA anchored on the substrate surface to produce a “grafting to” effect. The simple approach of immobilizing the thiocarbonyl-thioether compound on a hydrogen-terminated Si(100) surface via the radical stabilizing group (Z group) provided the stable, Si−C bonded CTA for the subsequent RAFT polymerization process (Scheme 1). Polymer−Si hybrids, consisting of covalently tethered brushes of 2-hydroxyethyl methacrylate (HEMA) polymer, methyl methacrylate (MMA) polymer, and their block copolymers with (2-dimethylamino)ethyl methacrylate (DMAEMA) were prepared (Scheme 1). The orthogonal surface chemistry or spatial ordering of the block sequence in the grafted diblock copolymers, produced by the interface-initiated RAFT polymerization, was revealed by X-ray photoelectron spectroscopy (XPS), as well as by Ar^+ beam etching and time-of-flight secondary ion mass spectroscopy (ToF−SIMS).

Results and Discussion

The use of hydrogenn-terminated silicon (Si−H) surfaces, instead of the Si/SiO_2 surfaces, allowed the preparation of polymer−Si hybrids with robust Si−C linkages.[34−36] A stable 4-vinylbenzyl chloride (VBC) monolayer was first immobilized on the Si−H surface, via UV-induced hydrosilylation of VBC with the Si−H bonds to give rise to the Si−VBC surface.[1,37] Figure 1a shows the wide scan and Cl 2p spectra of the Si−VBC surface. The Cl 2p core-level spectrum consists of a doublet with the binding energies (BEs) for the Cl $2p_{3/2}$ and Cl $2p_{1/2}$ peak components at about 199.7 and 201.5 eV, respectively, attributable to the covalently bonded chlorine species.[37] The XPS-derived surface [C]/[Cl] ratio of 9.0/1.0 is in complete agreement with the theoretical ratio of 9/1 for VBC. The static water contact angle has increased from about 73° for the Si−H surface to about 85° for the Si−VBC surface. On the basis of the VBC monolayer thickness of about 0.4 nm (as determined by ellipsometry), VBC density of 1.08 g/cm^3, and VBC molecular weight of 153 g/mol, the chloride density for the Si−VBC surface was estimated to be about 1.4 $units/nm^2$.

The Si−VBC surface with the coupled chain transfer agent (CTA) was prepared by the following: (i) reaction of the benzyl chloride functional group of the Si−VBC surface with sodium methoxide and elemental sulfur to form the sodium dithiobenzoate salt and (ii) conversion of the sodium dithiobenzoate salt to methoxycarbonylphenylmethyl dithiobenzoate (MCPDB) via reaction with methyl-α-bromophenylacetate (MBPA) to produce the Si−MCPDB surface.[38] Figure 1b shows the wide scan and S 2p spectra of the Si−MCPDB surface. The BEs for the S 2s and S 2p species are at about 228 and 163 eV, respectively. The S 2p core-level spectrum can be curve-fitted with two peak components with BEs at about 161.6 and 162.9 eV, attributable to the S═C and S−C species, respectively.[39] The chloride signal is no longer discernible in the XPS wide scan spectrum, indicating that the chlorobenzyl groups have been converted completely to the dithiobenzoate ester groups. Since the chloride density for the Si−VBC surface was about 1.4 $units/nm^2$, the CTA density for the Si−MCPDB surface was taken to be the same. The static water contact angle of the Si−MCPDB surface was determined to be about 76°, in comparison to about 85° for the starting Si−VBC surface.

In this work, 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA) were selected as the model monomers for the preparation of polymer−Si hybrids via interface-initiated reversible addition−fragmentation chain-transfer (RAFT) graft polymerization. In a typical polymerization reaction, the CTA, 2-phenylprop-2-yl dithiobenzoate (PDB), was added to a *N*,*N*-dimethylformamide (DMF) solution of monomer and 2,2-azobis(isobutyronitrile) (AIBN) in a molar ratio of monomer:PDB:AIBN = 2000:4:1. The introduction of free CTA in solution allows not only the control of polymerization in solution, but also help to maintain the well-defined character of the dormant chains grafted to the surface arising from the exchange reaction with the free chain redicals.[40] The

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* To whom correspondence should be addressed: Telephone +65-6874-2189. Fax +65-6779-1936. E-mail cheket@nus.edu.sg.

[†] Department of Chemical and Biomolecular Engineering, National University of Singapore.

[‡] Institute of Materials Research and Engineering, National University of Singapore.

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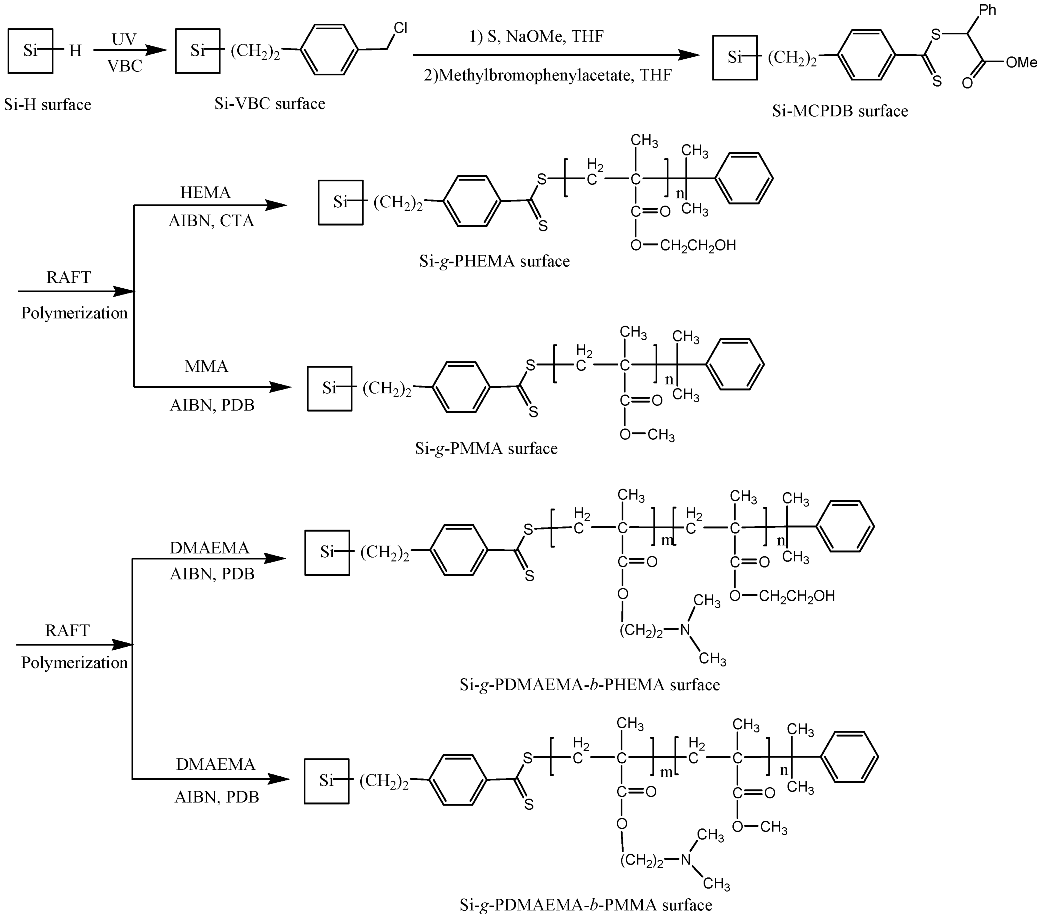
Scheme 1. Schematic Diagram Illustrating the Process of Interface-Initiated RAFT Graft Polymerization[a]



[a] Key: VBC = 4-vinylbenzyl chloride; HEMA = 2-hydroxyethyl methacrylate; CTA = chain transfer agent; THF = tetrahydrofuran; MCPDB = methoxycarbonylphenylmethyl dithiobenzoate; PHEMA = poly(2-hydroxyethyl methacrylate); AIBN = α,α′-azobis(isobutyronitrile); RAFT = reversible addition−fragmentation chain transfer; MMA = methyl methacrylate; PMMA = poly(methyl methacrylate); PDMAEMA = poly[(2-dimethylamino)ethyl methacrylate]; DMAEMA = (2-dimethylamino)ethyl methacrylate; PDB = 2-phenylprop-2-yl dithiobenzoate.

presence of grafted HEMA polymer (PHEMA) and MMA polymer (PMMA) on the Si−MCPDB surfaces (Si-*g*-PHEMA and Si-*g*-PMMA surfaces, respectively) was confirmed by XPS analysis.

Figure 1c shows the C 1s spectra of the Si-*g*-PHEMA surface obtained from 8 h of RAFT polymerization. The C 1s core-level spectrum of the Si-*g*-PHEMA surface can be curve-fitted into three peak components with BEs at about 284.6, 286.2, and 288.5 eV, attributable to the *C*−C/*C*−H, *C*−O, and O═*C*−O species, respectively.[41] The [C−H]:[C−O]:[O═C−O] molar ratio, as determined from the C 1s spectral component area ratio, is 3.3:2.5:1. This ratio deviates somewhat from the theoretical ratio of 3:2:1 for PHEMA, probably due to contributions of the underlying CTA to the aliphatic hydrocarbon species, as the PHEMA film thickness (∼6 nm, determined by ellipsometry) is less than the sampling depth of the XPS technique (∼7.5 nm in an organic matrix[42]).

Figure 1d shows the C 1s spectra of the Si-*g*-PMMA surface with a PMMA thickness of 5 nm, obtained from 8 h of RAFT polymerization. The C 1s spectrum consists of three peak components with BEs at 284.6 eV for the *C*−C/*C*−H species, 286.2 eV for the *C*−O species, and 288.5 eV for the O═*C*−O species.[43] The [C−H]:[C−O]:[O═C−O] molar ratio, as determined from the C 1s spectral component area ratio, is about 3.6:1.3:1. This ratio deviates somewhat from the theoretical ratio of 3:1:1, again probably due to contributions of the underlying CTA to the aliphatic hydrocarbon species, as in the case of the Si-*g*-PHEMA surface. When the silicon surface was grafted with a PHEMA layer, the static water angle of the surface had decreased substantially to about 39°, consistent with the hydrophilic nature of PHEMA. When grafted with a PMMA layer, the water contact angle of the surface has decreased to about 70°, which is comparable to that of the PMMA homopolymer (about 71°).[44]

The kinetics of PHEMA and PMMA growth from the Si−MCPDB surfaces via RAFT polymerization were investigated. An approximately linear increase in thickness of the grafted PHEMA and PMMA brushes on the surfaces with polymerization time was observed, as shown in Figure 2a. The results suggest that the chain growth from the Si−MCPDB surface was consistent with a “controlled” process. To confirm the existence of the dormant chains, interface-initiated RAFT block copolymerization of (2-dimethylamino)ethyl methacrylate (DMAEMA) was carried out, using the CTAs at the polymer−substrate interface as the macroinitiators to produce the respective PHEMA-*b*-PDMAEMA and PMMA-*b*-PDMAEMA diblock copolymers on the silicon surfaces.

The average cross-sectional area of methacrylate polymers[45] prepared by living radical polymerization is about 2 nm^2, the surface grafting efficiency of the present polymer, based on the grafting site density of 1.4 units/nm^2, is estimated to be about 36%. Thus, for the Si-*g*-PHEMA surface (PHEMA thickness = 6 nm) and the Si−PMMA surface (PMMA threickness = 5 nm) from 8 h of RAFT polymerization, the degrees of polymerization (DP) for the PHEMA and PMMA chains are estimated to be 64 and 70, respectively, based on the grafting

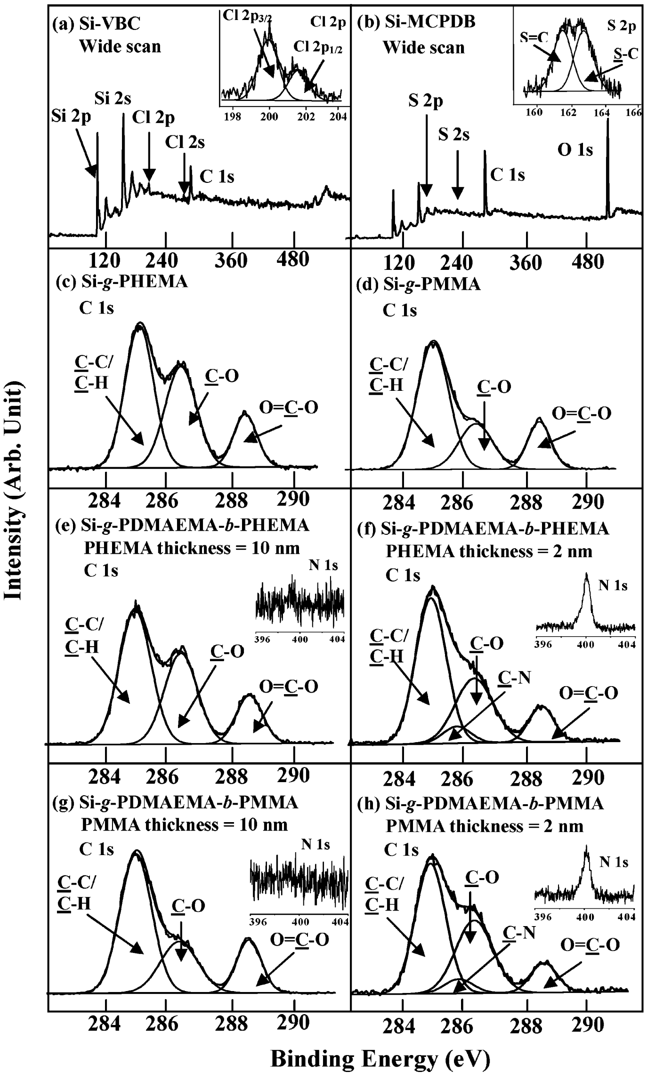


Figure 1. XPS core-level and wide-scan spectra of the (a) Si−VBC surface, (b) Si−MCPDB surface, (c) Si-*g*-PHEMA surface from 8 h of RAFT polymerization, (d) Si-*g*-PMMA surface from 8 h of RAFT polymerization, (e) Si-*g*-PDMAEMA-*b*-PHEMA surface from 16 h of RAFT block copolymerization using Si-*g*-PHEMA as the macro-CTA (PHEMA thickness = 10 nm), (f) Si-*g*-PDMAEMA-*b*-PHEMA surface from 16 h of RAFT block copolymerization using Si-*g*-PHEMA as the macro-CTA (PHEMA thickness = 2 nm), (g) Si-*g*-PDMAEMA-*b*-PMMA surface from 20 h of RAFT block copolymerization using Si-*g*-PMMA as the macro-CTA (PMMA thickness = 10 nm), (h) Si-*g*-PDMAEMA-*b*-PMMA surface from 20 h of RAFT block copolymerization using Si-*g*-PMMA as the macro-CTA (PMMA thickness = 2 nm). Reaction conditions: [monomer]:[PDB]:[AIBN] = 2000:4:1 in dry DMF at 75°C on CTA immobilized hydrogen-terminated Si(100) (Si−H) substrate; VBC = 4-vinylbenzyl chloride; AIBN = α,α′-azobis-(isobutyronitrile); PDB = 2-Phenylprop-2-yl dithiobenzoate; MCPDB = methoxycarbonylphenylmethyl dithiobenzoate; PHEMA = poly(2-hydroxyethyl methacrylate); PMMA = poly(methyl methacrylate); PDMAEMA = poly[(2-dimethylamino)ethyl methacrylate]; CTA = chain transfer agent.

efficiency of 36% and bulk PHEMA and PMMA polymer densities of 1.15 and 1.17 g/cm^3, respectively. The molecular weights of the grafted PHEMA and PMMA are calculated to be about 8300 and 7000, which are comparable to the values measured by gel permeation chromatography (GPC) for the PHEMA (M_n = 8600, PDI(M_w/M_n) = 1.15) and PMMA (M_n = 7200, PDI = 1.22) homopolymers recovered from the reaction mixtures at the RAFT polymerization time of 8 h (Figure 2b). Thus, the "grafting to" efficiency, at least in the initial stage, is comparable that of the "grafting from" process.

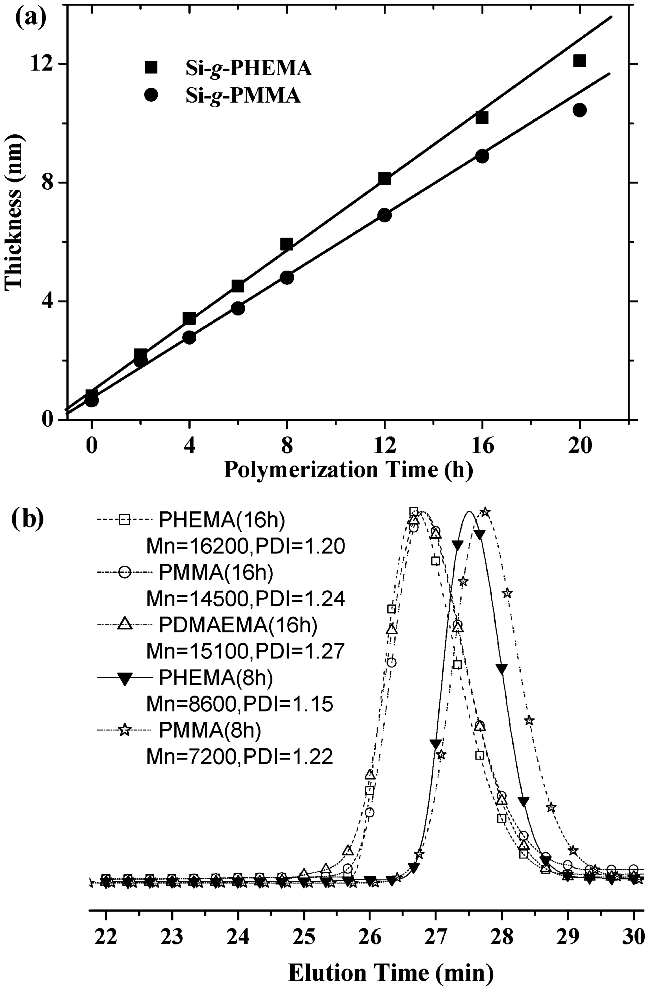


Figure 2. (a) Dependence of the grafted polymer film thickness on the RAFT polymerization time for the Si-*g*-PHEMA and Si-*g*-PMMA surfaces; (b) gel permeation chromatography (GPC) traces of the PHEMA, PMMA and PDMAEMA homopolymers recovered from the reaction mixtures after 8 h and 16 h of RAFT polymerization. Reaction conditions: [monomer]:[PDB]:[AIBN] = 2000:4:1 in dry DMF at 75°C on CTA immobilized hydrogen-terminated Si(100) (Si−H) substrate. AIBN = α,α′-azobis(isobutyronitrile); PDB = 2-Phenylprop-2-yl dithiobenzoate; PHEMA = poly(2-hydroxyethyl methacrylate); PMMA = poly(methyl methacrylate); PDMAEMA = poly[(2-dimethylamino)-ethyl methacrylate]; CTA = chain transfer agent.

Figure 2b also shows the GPC traces of the resulting PHEMA, PMMA, and PDMAEMA homopolymers recovered from the reaction mixtures after 16 h of RAFT polymerization. The M_n's of the PHEMA, PMMA, and PDMAEMA homopolymers are are 16200, 14500, and 15100, respectively. The corresponding PDIs are 1.19, 1.23, and 1.25. The DPs for the grafted PHEMA and PMMA chains (RAFT polymerization = 16 h) on Si surface are estimated to be 106 (film thickness = 10 nm) and 119 (film thickness = 8.5 nm), respectively. Thus, the molecular weights of the grafted PHEMA and PMMA are estimated to be about 13700 and 12600, which are slightly lower than those of the homopolymers recovered from the solutions.

Figure 1e shows the C 1s and N 1s spectra of the Si-*g*-PDMAEMA-*b*-PHEMA surface (from an RAFT block copolymerization time of 16 h and with a PDMAEMA thickness of about 4 nm), using the Si-*g*-PHEMA interface, with a PHEMA thickness of about 10 nm prepared from 16 h of RAFT polymerization, as the macro-CTA. The C 1s spectrum of the surface can be curve-fitted with three peak components with BEs at about 284.6, 286.2, and 288.5 eV, attributable to the *C*−C/*C*−H, *C*−O, and O=*C*−O species,[45] respectively. The

N 1s signal at the BE of about 399.8 eV, attributable to the amino group of the underlying PDMAEMA, was not discernible. Thus, the outer surface of Si-*g*-PDMAEMA−B−PHEMA is dominated by PHEMA. Figure 1f shows the C 1s and N 1s spectra of the Si-*g*-PDMAEMA-*b*-PHEMA surface (from an RAFT block copolymerization time of 16 h and with a PDMAEMA film thickness of about 4 nm), using the Si-*g*-PHEMA interface, with a PHEMA film thickness of about 2 nm prepared from 2 h of RAFT polymerization, as the macro-CTA. Since the PHEMA film thickness (about 2 nm) is considerably below the sampling depth of the XPS technique (about 7.5 nm in an organic matrix[42]), the N 1s signal from the underlying PDMAEMA is discernible. Furthermore, a new *C*-N peak component at the BE of about 285.6 eV[46] is also discernible in the C 1s core-level spectrum, suggesting significant contribution of the underlying PDMAEMA layer to the C 1s signal of the block copolymer.

Figure 1g shows the C 1s and N 1s spectra of the Si-*g*-PDMAEMA-*b*-PMMA surface (from an RAFT block copolymerization time of 20 h and with a PDMAEMA film thickness of about 3 nm), using the Si-*g*-PMMA interface, with a PMMA thickness of about 10 nm prepared from an RAFT polymerization time of 20 h, as the macro-CTA. The spectrum consists of three peak components with BEs at 284.6 eV for the *C*−C/*C*−H species, 286.2 eV for the *C*−O species, and 288.5 eV for the O═*C*−O species,[45] and with a peak component area ratio of about 3:1:1, characteristic of PMMA. The N 1s signals from the underlying PDMAEMA at the BE of about 399.8 eV was again not discernible. Figure 1h shows the C 1s and N 1s spectra of the Si-*g*-PDMAEMA-*b*-PMMA surface (after an RAFT block copolymerization time of 20 h and with a PDMAEMA film thickness of about 3 nm), using the Si-*g*-PMMA interface, with a PMMA film thickness of about 2 nm prepared from 2 h of RAFT polymerization, as the macro-CTA. The N 1s signal and the *C*-N species from the underlying PDMAEMA are also discernible, because the PMMA film thickness (about 2 nm) is below the sampling depth of the XPS technique. From the thickness of PDMAEMA layer in the block copolymers, 4 nm for Si-*g*-PDMAEMA-*b*-PHEMA and 3 nm for Si-*g*-PDMAEMA-*b*-PMMA, the DPs of PDMAEMA in the block copolymers are estimated to be 34 and 26, respectively, which correspond to molecular weights of 5300 and 4100. In comparison with the higher molecular weight (15100, see above) of the PDMAEMA homopolymer recovered from the solution after 16 h, steric effect in the thick block copolymer films has eventually prevented effective chain transfer and the "grafting to" process at the substrate−polymer interface.

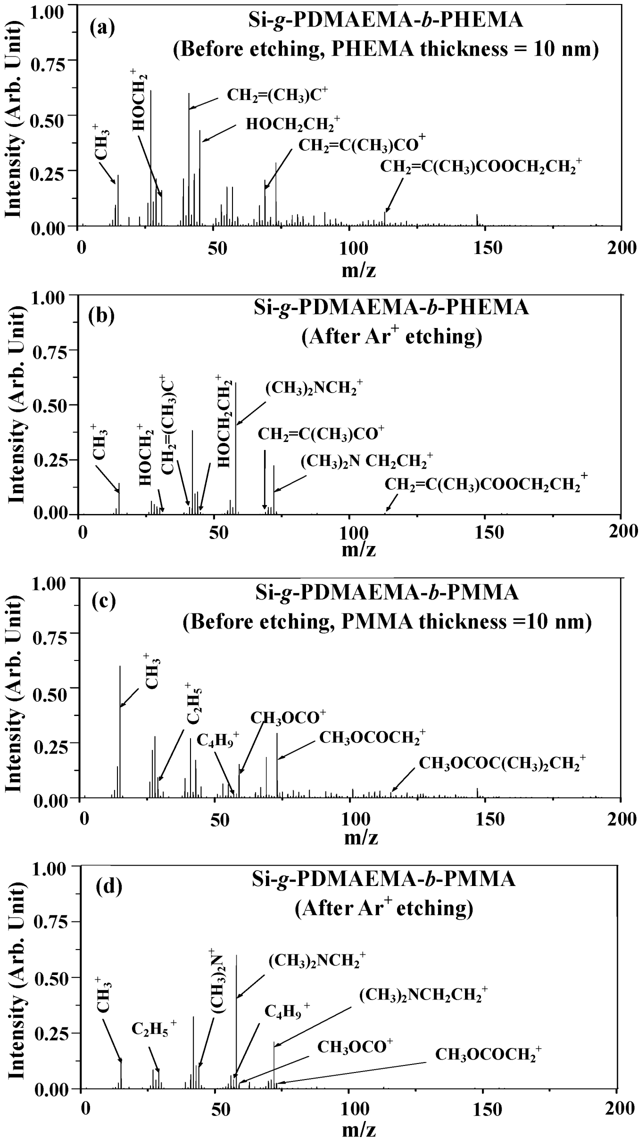


Figure 3. Positive ToF−SIMS spectra of (a) Si-*g*-PDMAEMA-*b*-PHEMA before etching (PHEMA thickness = 10 nm), (b) Si-*g*-PDMAEMA-*b*-PHEMA after Ar^+ beam etching for 200 s, (c) Si-*g*-PDMAEMA-*b*-PMMA before etching (PMMA thickness = 10 nm), (d) Si-*g*-PDMAEMA-*b*-PMMA after Ar^+ beam etching for 200 s. The Si-*g*-PDMAEMA-*b*-PHEMA surface was from 16 h of RAFT block copolymerization using Si-*g*-PHEMA as the macro-CTA (PHEMA thickness = 10 nm). The Si-*g*-PDMAEMA-*b*-PMMA surface was from 20 h of RAFT block copolymerization using Si-*g*-PMMA as the macro-CTA (PMMA thickness = 10 nm). PHEMA = poly(2-hydroxyethyl methacrylate); PMMA = poly(methyl methacrylate); PDMAEMA = poly[(2-dimethylamino)ethyl methacrylate].

The orthogonal surface chemistry or spatial ordering of the block sequence in the grafted PDMAEMA-*b*-PHEMA and PDMAEMA-*b*-PMMA copolymers on the Si surface was also characterized by time-of-flight secondary-ion mass spectrometry (ToF−SIMS). Parts a and b of Figure 3 show the respective positive ToF−SIMS spectra of the Si-*g*-PDMAEMA-*b*-PHEMA surface (same sample as that of Figure 1e) before and after depth profiling by Ar^+ beam for 200 s. In Figure 3a, only mass fragments from PHEMA are found. The fragments at *m*/*z* 31 is assigned to $HOCH_2^+$, at 41 to $CH_2{=}(CH_3)C^+$, at 45 to $HOCH_2CH_2^+$, at 69 to $CH_2{=}(CH_3)CO^+$, and at 113 to $CH_2{=}(CH_3)COOCH_2CH_2^+$. Since the thickness of PHEMA was about 10 nm, mass fragments from the underlying PDMAEMA was not found. However, after etching with the Ar^+ ion beam (Figure 3b), the signal intensity of the mass fragments from PHEMA became weak and mass fragments from PDMAEMA were found. The fragment at *m*/*z* 58 is assigned to $(CH_3)_2NCH_2^+$ and at 72 to $(CH_3)_2NCH_2CH_2^+$ of PDMAEMA, respectively. Similar results were obtained for the Si-*g*-PDMAEMA-*b*-PMMA surfaces. Parts c and d of Figure 3 show the positive Tof-SIMS spectra of the Si-*g*-PDMAEMA-*b*-PMMA surface (same sample as that of Figure 1g) before and after depth profiling by Ar^+ beam for 200 s. In Figure 3c, only mass fragment signals from PMMA are found. Mass fragment at *m*/*z* at 29, 57, 59, 73, and 115 are assigned to the $C_2H_5^+$, $C_4H_9^+$, CH_3OCO^+, $CH_3OCOCH_2^+$ and $CH_3OCO(CH_3)_2CH_2^+$ fragments, respectively. In Figure 3d, the additional fragments at *m*/*z* at 44, 58, and 72 are assigned to the $(CH_3)_2N^+$, $(CH_3)_2NCH_2^+$, and $(CH_3)_2NCH_2CH_2^+$ species of the PDMAEMA layer after the surface has been etched by ion beam. These results indicate that the "living chain ends" containing the CTA and tethered on the Si surface have allowed reactivation during the subsequent interfacial block copolymerization to give rise to the corresponding diblock copolymer brushes.

The PDMAEMA layer beneath the thick (greater than the probing depth of the XPS technique) PHEMA and PMMA layers in the block copolymers was also revealed by the attenuated total reflectance Fourier transform infrared (ATR−FTIR) spectroscopy (see Supporting Information). The appearance of characteristic adsorption bands associated with the asymmetric and symmetric stretches of the methyl groups in $-N(CH_3)_2$ (2820 and 2770 cm^{-1}, respectively) indicates the presence of PDMAEMA blocks.

Experimental Section

Details on materials and surface characterization are given in the Supporting Information.

Immobilization of the Chain Transfer Agent (CTA) on the Hydrogen-Terminated Si(100) (Si—H) Surface. The procedures for the immobilization of 4-vinylbenzyl chloride (VBC, 90%) on the hydrogen-terminated Si(100) (Si−H) surface via UV-induced hydrosilylation to produce the Si−VBC surface had been described earlier.[1,37] The Si−VBC substrate was introduced into a round-bottom flask containing 0.8 g of elemental sulfur (99%) and 1.35 g of sodium methoxide (99%) in 50 mL of tetrahydrofuran (99.5%). The reaction was left overnight at 70°C. The substrate was removed and washed with warm toluene, warm THF, methanol, and warm H_2O, in that order. The substrate was dried by pumping under reduced pressure. The dried substrate was then immersed in a solution containing 5.0 g of methyl-α-bromophenylacetate (MBPA, 97%) in 15 mL of tetrahydrofuran to convert the sodium dithiobenzoate salt on the surface to methoxycarbonylphenylmethyl dithiobenzoate (MCPDB).[38] The solution was refluxed for 12 h. The substrate was removed and washed with toluene, warm THF, a mixture of water, and THF (1:1, v:v), warm THF and dichloromethane, in that order. The CTA-coupled Si−H (Si−MCPDB) substrate was then dried by pumping under reduced pressure.

Synthesis of Polymer Brushes on Si—MCPDB via Interface-Initiated RAFT Polymerization. For the graft polymerization of the 2-hydroxyethyl methacrylate (HEMA) on the Si-MCPDB surface, HEMA (2.67 mL, 22 mmol, 97%), 2-phenylprop-2-yl dithiobenzoate (PDB) (11.98 mg, 0.044 mmol, 99+%), and 2,2′-azobis(isobutyronitrile) (AIBN) (1.8 mg, 0.011 mmol, 97%) were added to 2.5 mL of dried DMF (99.5+%) in a Pyrex tube. The mixture was stirred and degassed with argon for 30 min. The Si−MCPDB substrate was then introduced into the reaction mixture. The reaction tube was sealed under argon and kept in a 75°C oil bath for 2−20 h. After the reaction, the silicon substrate with surface grafted poly(2-hydroxyethyl methacrylate) (PHEMA) (the Si-*g*-PHEMA surface) was removed from the reaction mixture and washed thoroughly with excess DMF for 24 h. It was subsequently rinsed with distilled water and acetone. The substrate was dried for 10 h by pumping under reduced pressure. The PHEMA homopolymer was recovered by precipitation of the reaction mixture in diethyl ether.

The process for surface-initiated RAFT polymerization of poly(methyl methacrylate) (MMA, 99%) on the Si−MCPDB surface was similar to that described for the preparation of the Si-*g*-PHEMA hybrid. A MMA:PDB:AIBN molar ratio of 2000:4:1 was also used. After the reaction, the silicon substrate with surface grafted PMMA (Si-*g*-PMMA surface) was removed from the reaction mixture and washed thoroughly with excess DMF for 24 h. It was subsequently rinsed with distilled water and chloroform. The substrate was then dried for 10 h by pumping under reduced pressure. The PMMA homopolymer was recovered by precipitation of the reaction mixture in methanol.

Synthesis of the Diblock Polymer Brushes on the Silicon Surfaces via Interface-Initiated RAFT Polymerization. The Si-*g*-PHEMA or Si-*g*-PMMA interface was used as the macro-CTA to prepare diblock copolymer brushes. The procedures were similar to those used for the synthesis of the Si-*g*-PHEMA or Si-*g*-PMMA brushes, except that 2.32 mL (22 mmol) of the (2-dimethylamino)-ethyl methacrylate (DMAEMA, 98%) monomer and a piece of freshly prepared Si-*g*-PHEMA or Si-*g*-PMMA wafer were used to produce the Si-*g*-PDMAEMA-*b*-PHEMA or Si-*g*-PDMAEMA-*b*-PMMA surface. After an RAFT block copolymerization time of 12 h, the substrate was removed from the reaction mixture and washed with excess DMF for 24 h. It was then rinsed with excess THF and ethanol. The substrate was dried for 10 h by pumping under reduced pressure. The PDMAEMA homopolymer was recovered by precipitation of the reaction mixture in hexane.

Supporting Information Available: Text giving the materials description and experimental procedures for surface characterization by XPS, ATR−FTIR spectroscopy, ellipsometry, and ToF−SIMS and figures showing the ATR−FTIR spectra of the polymer-grafted Si surfaces and AFM results of the Si−H, Si−MCPDB, Si-*g*-PHEMA and Si-*g*-PMMA surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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